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Identification, distribution and possible origins of sulfates in Capri Chasma (Mars), inferred from CRISM data

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[1] CRISM is a hyperspectral imager onboard the Mars Reconnaissance Orbiter (MRO; NASA, 2005) which has been acquiring data since November 2006 and has targeted hydrated minerals previously detected by OMEGA (Mars Express; ESA, 2003). The present study focuses on hydrated minerals detected with CRISM at high spatial resolution in the vicinity of Capri Chasma, a canyon of the Valles Marineris system. CRISM data were processed and coupled with MRO and other spacecraft data, in particular HiRISE (High Resolution Science Experiment, MRO) images. Detections revealed sulfates in abundance in Capri, especially linked to the interior layered deposits (ILD) that lie in the central part of the chasma. Both monohydrated and polyhydrated sulfates are found at different elevations and are associated with different layers. Monohydrated sulfates are widely detected over the massive light-toned cliffs of the ILD, whereas polyhydrated sulfates seem to form a basal and a top layer associated with lower-albedo deposits in flatter areas. Hydrated silicates (phyllosilicates or opaline silica) have also been detected very locally on two mounds about a few hundred meters in diameter at the bottom of the ILD cliffs. We suggest some formation models of these minerals that are consistent with our observations.

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1. Introduction

[2] Sulfates were discovered by the spectral imager OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité), onboard Mars Express, at various locations on Mars [Gendrin *et al.*, 2005]. Sulfates are abundant in the Valles Marineris area, near the northern cap in Utopia Planitia, and locally in the plains of Terra Meridiani [Bibring *et al.*, 2006]. They have also been discovered in situ by the two Mars Exploration Rovers, Spirit and Opportunity, in Gusev Crater and Meridiani Planum [Squyres *et al.*, 2004; Grotzinger *et al.*, 2005; Wang *et al.*, 2006]. In all these locations, they are detected in association with sedimentary deposits. Therefore, all these previous missions have proposed that the sulfate occurrence is strongly linked with the water and climate history of Mars. The sulfates have been interpreted to represent a global climate change on Mars from the Noachian through the

Hesperian, marked by a change from alkaline to acidic pH conditions and a transition from a wetter to a drier environment [Bibring *et al.*, 2006]. Observations obtained with the imaging spectrometer CRISM (the Compact Reconnaissance Imaging Spectrometer for Mars) onboard the MRO (Mars Reconnaissance Orbiter) spacecraft enabled us to refine the distribution and mineralogical composition of the hydrated minerals previously detected by OMEGA. With 544 channels acquiring images at 6.55 nm/channel between 0.362 and 3.92 μm in targeted mode, CRISM can resolve many diagnostic mineral features. Its spatial resolution ranges from 18 to 36 m per pixel in hyperspectral mode, which is ~ 15 times better than OMEGA resolution [Murchie *et al.*, 2007]. CRISM is coaligned with other instruments on MRO; CTX (Context Camera) and HiRISE (High Resolution Imaging Science Experiment) provide high-resolution images (up to 25 cm per pixel) in conjunction with CRISM observations [Malin *et al.*, 2007; McEwen *et al.*, 2007]. The association of all these data facilitates the precise identification of geological units and layers carrying a given spectral signature.

[3] In the equatorial area, sulfate signatures are correlated to light-toned layered deposits, named interior layered deposits (ILD) [Gendrin *et al.*, 2005]. ILD are massive, stratified, bright deposits often found in the central part of most of Valles Marineris chasmata [Lucchitta *et al.*, 1994; Flahaut *et al.*, 2010]. The present study focuses on these deposits in a part of the Valles Marineris system called Capri

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Chasma. Valles Marineris is an important area to study as it represents the largest sulfate reservoir known on Mars and is associated with the enigmatic ILD. Indeed, the ILD origin and age are still unknown [Flahaut et al., 2010]. Proposed genetic mechanisms for the ILD include mass wasting of wallrocks [Nedell et al., 1987], aeolian [Peterson, 1981], volcanic [Chapman and Tanaka, 2001; Komatsu et al., 2004], or lacustrine [McCauley, 1978; Komatsu et al., 1993; Lucchitta et al., 1994] processes. Edgett and Malin [2003] have suggested that ILD could be exhumed remnants of preexisting Noachian deposits. Various hypotheses for the formation of sulfates in the area of Capri Chasma and in Valles Marineris in general, and their consequences on the ILD formation scenarios, are presented and discussed herein.

2. Geological Setting

[4] Valles Marineris is the largest canyon on the surface of Mars. Its troughs are thought to have formed by tectonic extension and/or subsurface removal of groundwater. [Schultz, 1991; Lucchitta et al., 1992; Peulvast and Masson, 1993; Tanaka, 1997; Weitz et al., 2003]. Capri Chasma, the largest of the Valles Marineris chasmata, is located at the outlet of this canyon system as a continuation of Coprates Chasma and at the head of the outflow channels that spread eastward [Flahaut et al., 2010]. Capri Chasma extends over an area greater than 650×350 km, its floor has an average elevation of -4000 m, and the surrounding plateaus are above $+2000$ m. The central part of the canyon is filled with ILD which formed three mesas of variable sizes. Capri Chasma's ILD have been described in detail by Flahaut et al. [2010]. The largest mesa, which is approximately 370×170 km wide and 3 km thick, exposes mainly massive light-toned material, where layering is difficult to observe. Lower albedo layers have also been observed at the bottom and at the top of the massive bright cliffs. All of the flat-topped mounds are covered with a dark fine dust, referred to as a *capping layer*, and present in other chasmata. An interesting feature in Capri Chasma is the association of layered deposits with typical morphologies of outflow channels such as catastrophic flow features and chaotic floors [Flahaut et al., 2010].

3. Methods

[5] A geographic information system (GIS) was built to gather data from different Martian missions. THEMIS visible and infrared day and night data from the Mars Odyssey spacecraft were used in association with the MOC (Mars Orbiter Camera) data from the Mars Global Surveyor mission and the HiRISE and CTX data from the MRO mission. The MOLA (Mars Orbiter Laser Altimeter) altimetry map, with a resolution of 300 m per pixel, was added to this image collection, providing topographic data. This combination of images offers full spatial coverage of the canyon. Hyperspectral and multispectral data from CRISM were used to determine mineralogical composition. CRISM data are calibrated to radiance and divided by the solar spectrum to obtain I/F. All the data are then corrected for atmospheric and photometric contribution and georeferenced with CAT v6.5, the publicly released version of the software. The atmospheric effects are removed using a ratio of a CRISM

scene of Olympus Mons, scaled to the same column density of CO_2 as in Mustard et al. [2008] and Pelkey et al. [2007]. Most of the mineralogical maps presented in this paper were derived using the spectral summary parameters of Pelkey et al. [2007] after reducing noise using the CIRRUS destriping and despiking function of CAT v6.5. For spectral features unavailable in Pelkey et al.'s [2007] spectral summary parameters, we constructed our own spectral parameters to map band depth. CRISM band depth maps were then integrated to our GIS and projected over HiRISE and CTX data. A list of all the CRISM and HiRISE data used in this study is given in Table 1.

4. Results

4.1. Identification of Signatures

[6] The region of investigation is shown in Figure 1, along with the distribution of hydrated minerals we have determined. All the CRISM hyperspectral data available as of 12 January 2009 in Capri Chasma were processed. Table 1 gathers all the CRISM observations which have relevant signatures. Twenty CRISM observations are located over the ILD material.

[7] Hydrated minerals are identified with CRISM by investigating the overtones and combinations of fundamental vibrational absorption features in the $1.0\text{--}2.6$ μm interval. Three hydrated phases have been detected in Capri Chasma: monohydrated sulfates, polyhydrated sulfates, and a hydrated silicate or silica (Figure 2).

[8] Strong absorption bands at 2.1 and 2.4 μm have been found in 20 CRISM observations, including 19 targeted over the ILD. The 2.4 μm feature is common to all sulfates and characterizes the SO_4 group vibrations within the structure (Figure 2). The shift of the bound water vibration from 1.9 to 2.1 μm in these spectra indicates the presence of a single water molecule in the sulfate structure. The combination of these two absorption features is diagnostic of monohydrated sulfates [Gendrin et al., 2005; Bibring et al., 2005]. The doublet shape of the 2.1 μm band, the position of its minimum reflectance at 2.13 μm , and the general shape of the spectra are consistent with Mg-monohydrated sulfates such as kieserite [Gendrin et al., 2005; Bishop et al., 2009]. The northern ILD mounds exhibit spectra with an additional sharp rise in reflectance between 1.0 μm and 1.3 μm which corresponds to a specific ferric iron absorption centered at 0.9 μm . This probably indicates a mixing of monohydrated sulfates with ferric oxides as seen by OMEGA in this part of the canyon [Bibring et al., 2007].

[9] The second spectral type detected is characterized by a broad 1.96 μm absorption band accompanied by a 2.4 μm band. The 1.9 μm absorption band occurs in all the minerals containing H_2O . The coupling of this band with a 2.4 μm drop is diagnostic of polyhydrated sulfates (Figure 2) [Gendrin et al., 2005; Bishop et al., 2009]. A weaker band around 1.4 μm is sometimes present, resulting from both H_2O and structural OH bending and stretching vibrations. In contrast to monohydrated sulfates, the cationic composition of these polyhydrated sulfates cannot be determined using CRISM spectra, since Mg-, Ca-, or other types of polyhydrated sulfates have spectra displaying absorption bands at very similar wavelength positions.

Table 1. List of All the CRISM Data, Main Targets, and Results^a

CRISM ID	Target	Results
FRT0000282F_07_IF164L_TRR2	ILD material	M
FRT0000B776_07_IF165L_TRR2		
FRT00003050_07_IF164L_TRR2	Bottom of the ILD	P
FRT000035BD_07_IF164L_TRR2	ILD material	M
FRT000085F9_07_IF164L_TRR2		
FRT000066F5_07_IF164L_TRR2	ILD material	M
FRT0000681A_07_IF164L_TRR2	Bottom of the ILD and ILD material	M + P + HS
FRT00007FAA_07_IF164L_TRR2		
FRT00007117_07_IF164L_TRR2	ILD material	Unusable
FRT00007F63_07_IF164L_TRR2	Walls	M
FRT00008CC0_07_IF164L_TRR2	ILD material	M
FRT0000A82E_07_IF164L_TRR2	ILD material	M + P
FRT0000B385_07_IF164L_TRR2	ILD material (impact crater)	M + P
FRT0000BB25_07_IF164L_TRR2	ILD material	M + P
FRT0000C152_07_IF164L_TRR2	ILD material	M + P
FRT0000C564_07_IF164L_TRR2	ILD material (impact crater)	M + P
FRT0000C678_07_IF164L_TRR2	ILD material	M
FRT0000C81D_07_IF164L_TRR2	ILD material	M + P
FRT0000D117_07_IF164L_TRR2	ILD material	M
FRT0000D3A4_07_IF164L_TRR2	ILD material (impact crater)	M + P
FRT0000D62D_07_IF164L_TRR2	ILD material	M + P
FRT0001070A_07_IF164L_TRR2	ILD material	M
HRL000072C9_07_IF181L_TRR2	Canyon floor/ILD material	
HRL0000A23F_07_IF181L_TRR2	Canyon floor/ILD material	M
HRL0000AF21_07_IF181L_TRR2	Canyon floor/ILD material	Unusable
HRL0000D770_07_IF181L_TRR2	ILD material	M + P
HRS00002F87_07_IF173L_TRR2	ILD material	M + P

^aM, monohydrated sulfates; P, polyhydrated sulfates; HS, hydrated silicates (phyllosilicates or opaline silica).

[10] The aforementioned detections are generally consistent with previous OMEGA detections [Gendrin *et al.*, 2005]. The capping layer, which covers the summit of ILDs, does not have any diagnostic absorption features. These roughly flat spectra could be explained by dust coverage.

[11] A third spectral type has been detected in a less important amount over the ILD material. In CRISM observation FRT00007FAA, two small mounds at the bottom of the ILD cliffs exhibit a strong 2.2 μm absorption band (Figure 3g). It is coupled with weaker 1.4 and 1.9 μm bands at the limit of detection (Figure 2). Comparison with the spectral library shows that this spectral type carries the signature of either Al phyllosilicates or hydrated silica. Indeed Si-OH bonds and Al-OH bonds have very similar vibrational features. Both have been reported in association with sulfates in some CRISM observations in other locations of Valles Marineris [Milliken *et al.*, 2008; Le Deit *et al.*, 2010]. Because the 2.2 μm absorption band is wide, with a doublet at 2.23 μm and 2.29 μm , we consider hydrated silica the most likely candidate. The position at 2.23 μm indicates that this silica is probably not highly altered [Milliken *et al.*, 2008]. The occurrence of this fresh hydrated silica associated with the ILD could provide clues about the formation of sulfates in Capri Chasma. The size of hydrated silica outcrops in Capri Chasma excludes their detection with OMEGA data.

4.2. Sulfate Distribution

[12] To understand the geological setting of the detected species, CRISM band depth maps were merged into our GIS with a variety of other images. Spectral signatures were generally considered as diagnostic of the presence of a mineral on the surface for absorption band depth values >1%. Because CRISM coverage is rather sparse (Figure 1a),

some of the regions are not mapped, but it does not mean that they do not have any spectral signatures.

[13] Figure 1 shows that sulfates are detected at the location of the ILDs in Capri Chasma, especially at their flanks. Sulfates have never before been detected in association with the chaotic floor of Capri Chasma. The monohydrated sulfate signatures are always associated with the same material: the steep outcrops of massive light-toned material forming the largest part of the ILD's edge (Figures 3a to 3c). Figure 3a shows the 2.1 μm band depth map projected over HiRISE data covering a portion of an outcrop on the north-facing flank of the ILD. Here the whole cliff is formed by a massive bright material, rich in monohydrated sulfates. Outcrops of the same material are found all around the ILD and are also enriched in monohydrated sulfates. These observations argue in favor of the bulk of the ILD being sulfate-rich. If we interpret the strength of the band depth only by a spatial mixture, the depth of the 2.1 μm band increases with the spatial content of monohydrated sulfates and so decreases with the abundance of the dust coverage or associated spectrally neutral material. We observed a relationship between the dust coverage in HiRISE images and the depth of the 2.1 μm band (Figures 3a to 3c). Some monohydrated sulfate signatures are found in the southwest wall of Capri Chasma (observation FRT00007F63), far from the ILD mesas. The material bearing this signature is light-toned and appears to be draped over the wall. It does not seem to form the bulk component of the wall or to be derived from it.

[14] The polyhydrated signatures are correlated with different morphologies from the monohydrated ones. The material carrying these signatures is composed of a lower albedo unit, that is finely layered, with coarse grains in some places (Figures 3d to 3f). In contrast to monohydrated sulfates, polyhydrated sulfates are more commonly found in associa-

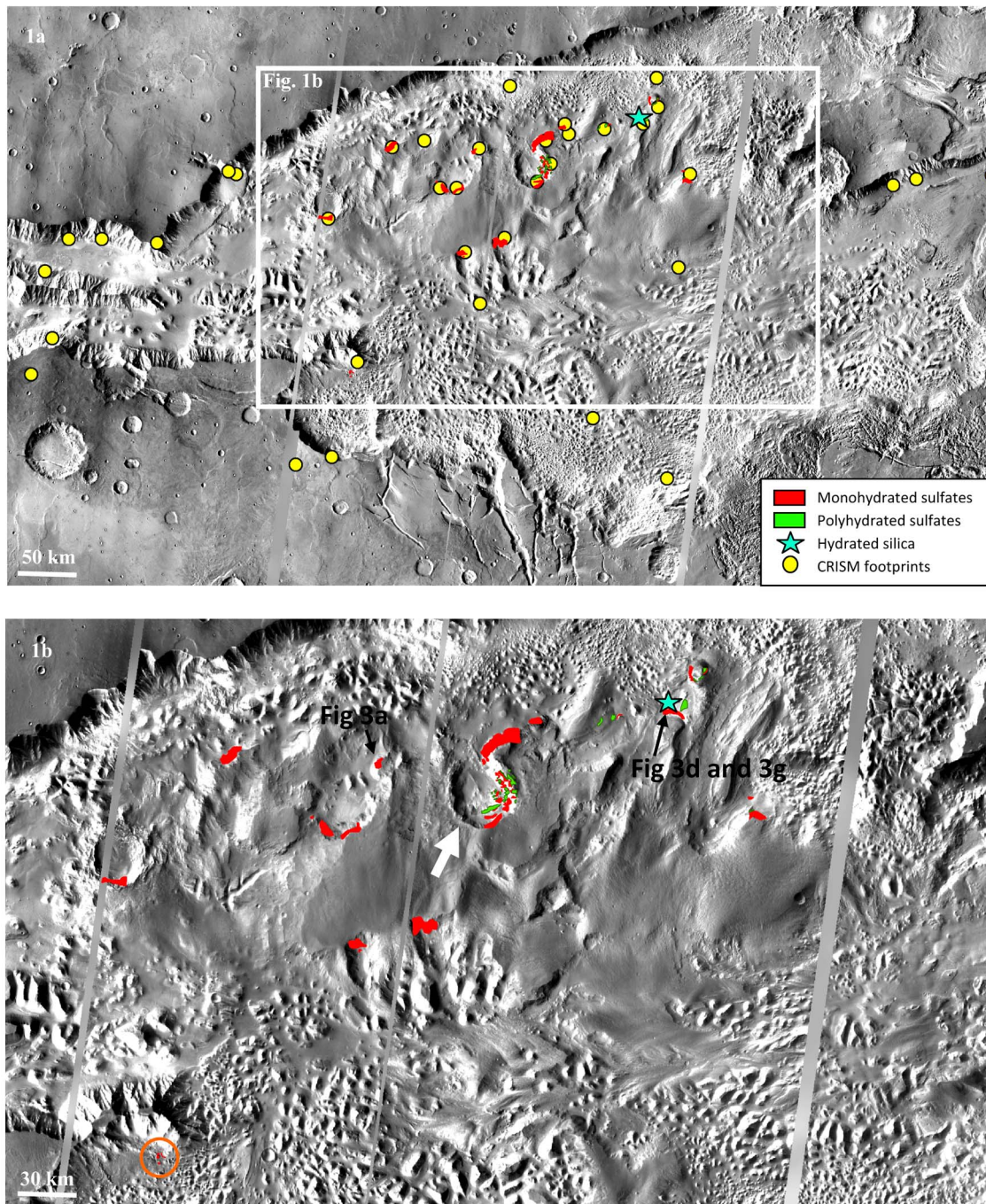


Figure 1. (a) Distribution of the main hydrated mineral detections in Capri Chasma (central longitude: 46.5°E, central latitude: 14.5°S). The white box indicates the location of Figure 1b. Yellow dots, CRISM footprints; red, monohydrated sulfates; green, polyhydrated sulfates; blue star, opaline silica, detected in a smaller amount. (b) Close-up on the main mesa of the ILD, showing sulfate detections above the flanks. The black arrows show the location of the close-up of Figures 3a, 3d, and 3g, while the white arrow points out the major impact crater presented in Figure 4. The orange circle points out the wall where monohydrated sulfates are detected as a superficial draping.

tion to flatter outcrops. In CRISM observation HRS00002F87, polyhydrated sulfates are detected on a material located above the monohydrated sulfates one. In other outcrops of the same mesa, as in the major impact crater affecting the ILD (Figure 4), the bottom material has 1.9 and 2.4 μm absorption bands, diagnostic of polyhydrated sulfates, while

the top material has strong 2.1 and 2.4 μm absorption bands, diagnostic of monohydrated sulfates. This can also be observed in other places of the canyon with hyperspectral (FRT00003050) or multispectral data. When outcropping, the material at the bottom of the massive light-toned cliffs of the ILD is enriched in polyhydrated sulfates (Figure 3d).

4.3. Vertical Distribution

[15] The vertical organization of sulfates in Capri Chasma deduced from OMEGA data revealed that polyhydrated sulfates were mainly laying underneath monohydrated sulfates [Gendrin *et al.*, 2005; Quantin *et al.*, 2005]. CRISM observations FRT0000D3A4, FRT0000B385, FRT0000C564,

FRT0000D62D, FRT00003050, and FRT00007FAA confirm these findings, with polyhydrated sulfates detected below -2400 m outside the main impact crater and often capped by monohydrated sulfates (Figures 4 and 5a). CRISM observations HRS00002F87, FRT0000C564, and FRT00003B85 also reveal polyhydrated sulfates that occur above the monohydrated sulfate-rich material at elevations above -1000 m (Figures 4 and 5a). The systematic extraction of elevation distribution on CRISM data shows that polyhydrated sulfates have a sharp bimodal distribution centered around -2500 and -500 meters (Figure 5b). On the contrary, monohydrated sulfates are more regularly distributed in elevation, as they are often detected all over high cliffs (Figure 1 and Figures 5a and 5b). It seems that polyhydrated sulfates form at least two groups of layers, one underlying layer and one top layer (with monohydrated sulfates in between) according to CRISM data.

[16] This alternation of polyhydrated and monohydrated sulfates has to be considered, taking its scale into account. Polyhydrated sulfates dominate the mineralogy of the bottom and top layers but are probably not the only component of these groups of layers. Spectrally flat material, such as halite, could be present, or small embedded layers of another material may be masked by the polyhydrated sulfate abundance, especially if these layers' extent is smaller than 20 m, which is CRISM's highest spatial resolution. Moreover, as shown in Figure 5b, polyhydrated sulfates are not completely absent within intermediate layers. It could be possible that there are more alternating layers within the ILD that are not seen because of the limited number of CRISM data available or because of their extents with respect to the resolution of the imager. Modifications of the layers by faulting, tilting, or sliding may also have affected the observed distribution, even if the layers are roughly horizontal.

5. Discussion

5.1. Sulfate Distribution

[17] Our results show that both monohydrated and polyhydrated sulfates are found in abundance in Capri Chasma. They are associated with the ILD that have filled the canyon after its opening [Flahaut *et al.*, 2010]. Their distribution raises the question whether they are the bulk component of the ILD. As spectral imagers only investigate the first few micrometers of the surface [Murchie *et al.*, 2007], we cannot exclude that sulfates were simply made by superficial weathering and are thus a simple coating independent of the bulk of the rock. In this case, the ILD material must be made

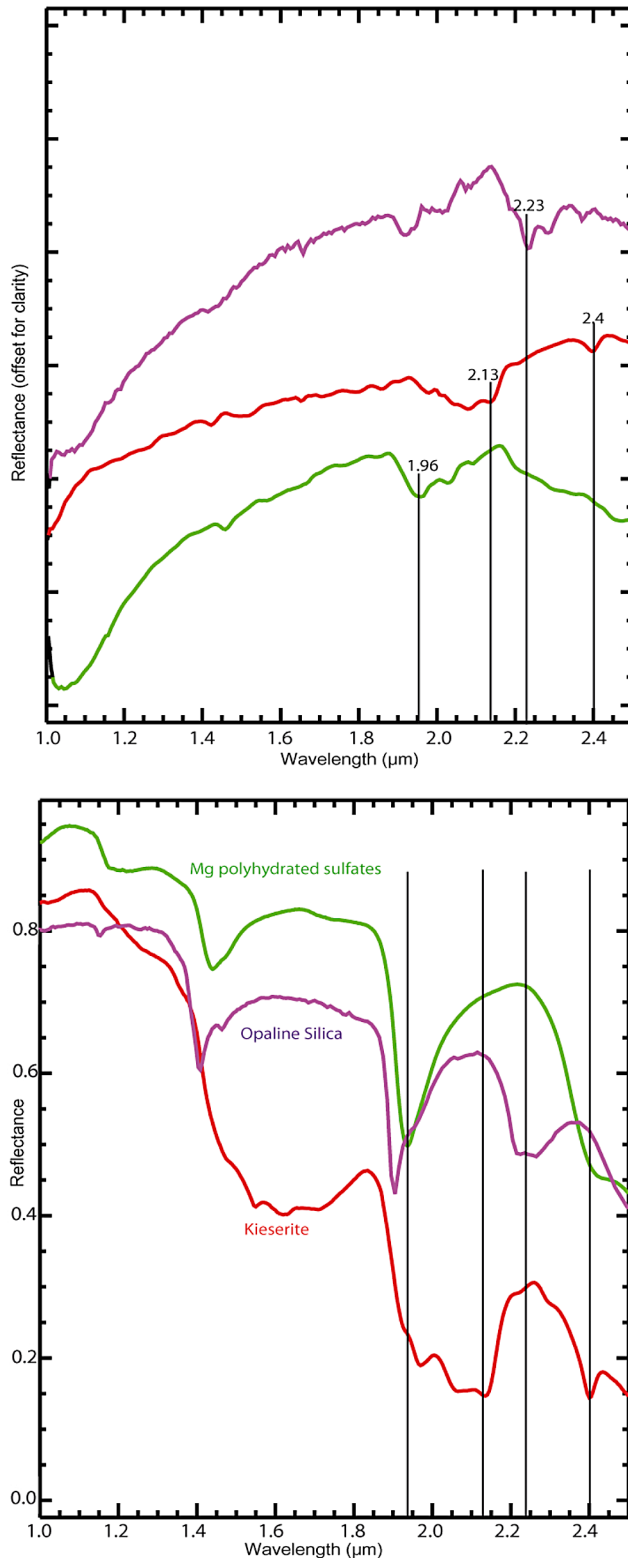


Figure 2. (top) CRISM ratioed spectra of the three spectral types we identified in Capri Chasma. Spectra were ratioed with a dust spectrum, acquired on the same CRISM observation. Monohydrated sulfates are identified on the red spectrum with diagnostic 2.1 and 2.4 μm spectral features. Polyhydrated sulfates are identified on the green spectrum with diagnostic 1.9 and 2.4 μm spectral features. The purple spectrum presents a 2.2 μm doublet-shaped band that is characteristic of hydrated silica. (bottom) Laboratory spectra of the USGS spectral library are given for comparison. Red: kieserite (i.e., magnesium monohydrated sulfates), green: magnesium polyhydrated sulfates, purple: opaline silica.

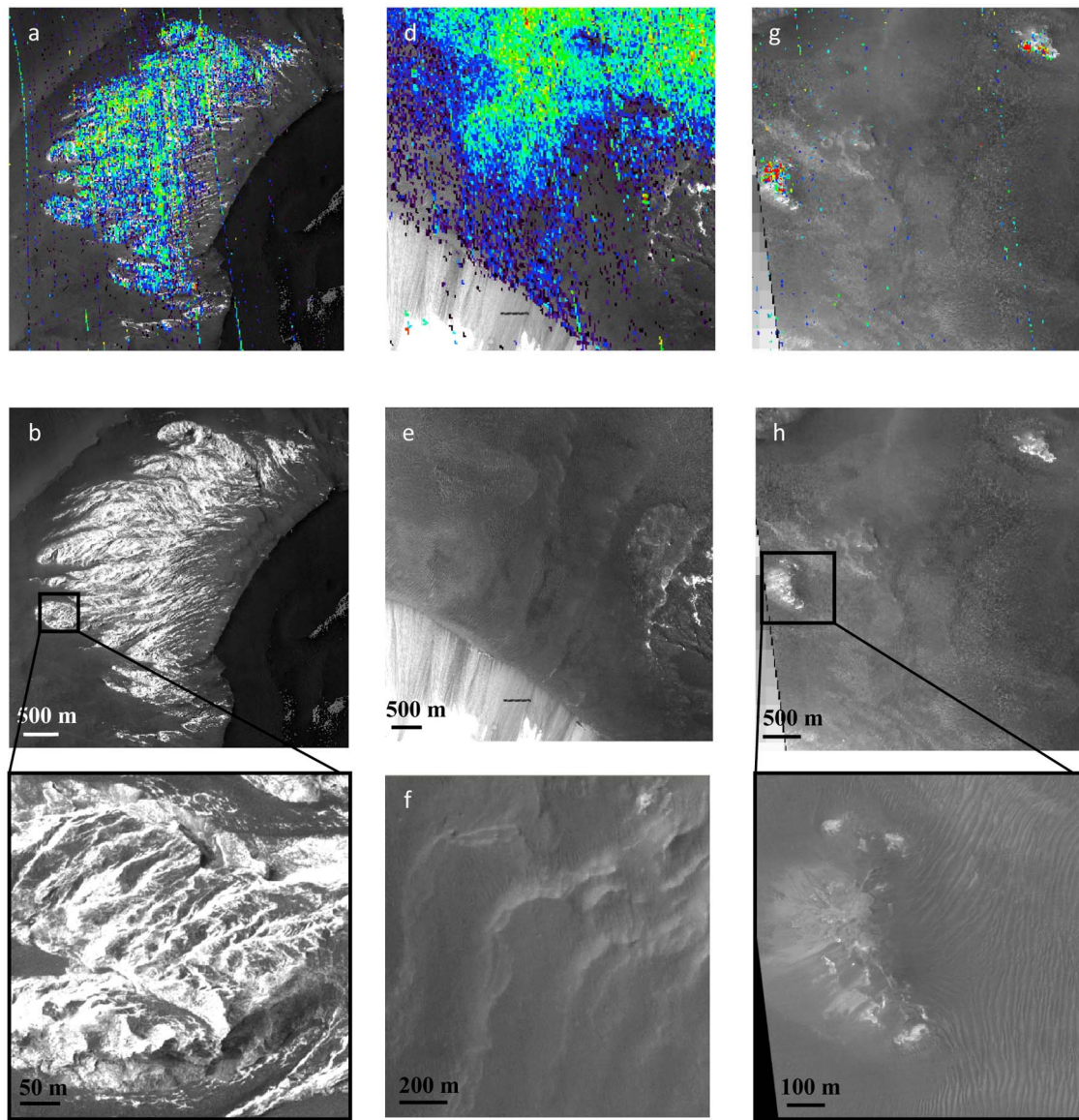


Figure 3. Band depth maps (in a rainbow scale: blue is low, red is high) and HiRISE and CTX views associated with previous detections. (a) BD2100 of CRISM observation FRT000035BD is projected over HiRISE PSP_1772_1665_RED. (stretched values: 0.027–0.050). (b) Portion of HiRISE PSP_1772_1665_RED: Monohydrated sulfates are always associated with bright massive outcrops on ILD flanks. (c) Close-up of Figure 3b. (d) BD1900 of CRISM observation FRT00007FAA is projected over HiRISE PSP_4396_1675_RED and CTXP01_001376_1676_XI_12S046W (stretched values: 0.007–0.025). (e) Portion of CTX P01_001376_1676_XI_12S046W: Polyhydrated sulfates are more commonly detected over these flatter and lower-albedo layers. (f) Close-up of some polyhydrated sulfates. (g) 2.23 band depth map of CRISM observation FRT00007FAA is projected over HiRISE PSP_4396_1675_RED (stretched values: 0.005–0.013). (h) Portion of HiRISE PSP_4396_1675_RED: Hydrated silica is locally found on 100 m scale mounds. (i) Close-up of Figure 3h.

of a particular material more likely to be altered into sulfates than the wallslopes of Valles Marineris that do not bear any sulfate signatures. Nevertheless, sulfates are more likely to correspond to the bulk component of the ILD, rather than to a superficial alteration crust [Gendrin *et al.*, 2005]. This idea is supported by the fact that sulfates are only detected in association with the ILD, and over several flanks of the same ILD mesa, at similar elevations. Furthermore, large impact craters do not show any ILD outcrops, suggesting

that ILD were formed more recently [Malin and Edgett, 2000]. However, as it is unlikely that superficial sulfates formed in the current climatic conditions on Mars, the exposed sulfates must be old bedrock.

[18] Comparison with HiRISE data show that monohydrated sulfates are detected over massive bright outcrops of layered material. An underlying unit, displaying a lower albedo and coarse grains, enriched in polyhydrated sulfates, is observed in some locations, such as the deepest layers

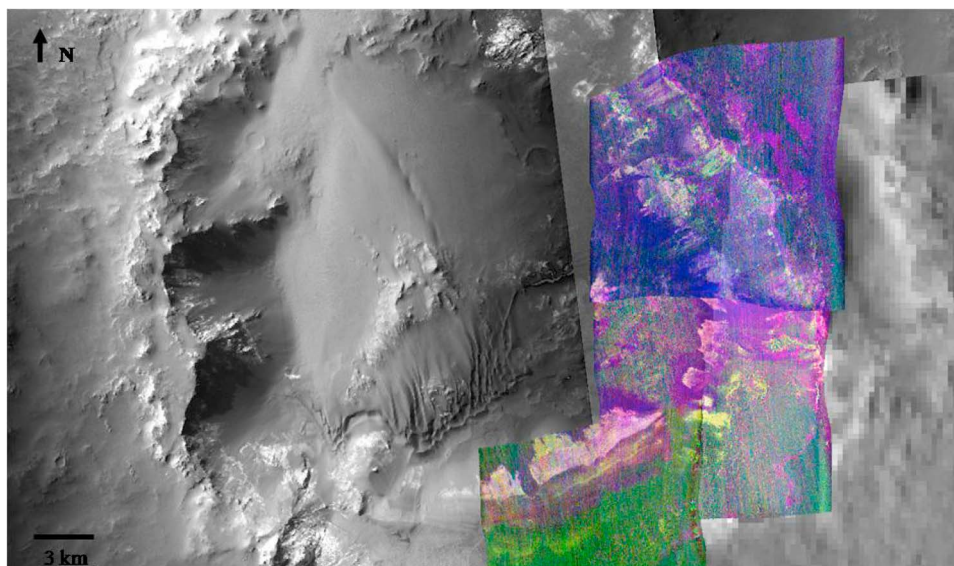


Figure 4. RGB composite of summary products BD1900 (blue), BD2100 (green), and BD2400 (red) on CRISM observations FRT0000B385 (stretched values: R:0.004–0.059, G:0–0.042, B:0.007–0.037), FRT0000C564 (stretched values: R:0.024–0.071, G:0.001–0.051, B:0.006–0.028), and FRT0000D3A4 (stretched values: R:0.004–0.055, G:0–0.035, B:0–0.026). These observations were acquired on the largest impact crater that is affecting the ILL in Capri Chasma (location shown with a white arrow in Figure 1b). CRISM data are overlain on CTX and HiRISE data. Polyhydrated sulfates appear in purple, monohydrated ones in yellow. Polyhydrated sulfates are detected on the floor of the crater, and at the very top of the crater walls. Monohydrated sulfates are found in between. There might be more interbedded alternation of polyhydrated and monohydrated sulfates, but dust coverage and avalanches make the observations difficult to interpret precisely.

exposed in the major impact crater emplaced on ILL (Figure 4). Polyhydrated sulfates are also detected stratigraphically above monohydrated sulfates in a few locations. Coupling of polyhydrated and monohydrated sulfates have been reported in several other chasmata of Valles Marineris [Quantin *et al.*, 2005; Bishop *et al.*, 2009; Murchie *et al.*, 2009a]. However, Capri Chasma is a unique case presenting the following large-scale alternation of hydration state of sulfates: polyhydrated sulfates, monohydrated sulfates, and polyhydrated sulfates again. Alternations have already been reported in other canyons of Valles Marineris [Roach *et al.*, 2009], but at a smaller scale corresponding to a decametric alternation of layers. Other kilometeric alternations of different hydration states of sulfates were previously detected in Melas Chasma or in Juventae Chasma, where polyhydrated sulfates are either below [Quantin *et al.*, 2005] or above [Bishop *et al.*, 2009; Murchie *et al.*, 2009a] monohydrated sulfates, but not both as in Capri Chasma.

5.2. Sulfate Hydration State

[19] The origin and distribution of the two hydration states of sulfates, monohydrated and polyhydrated, is subject to discussion. First of all, we have to consider the possibility that the hydration states of sulfates reflect state changes after formation. According to Roach *et al.* [2009], the occurrence of polyhydrated sulfates can be explained by the rehydration of monohydrated sulfates under wetter and colder conditions. This could have become possible lately under large-scale obliquity variations. Considering we have at least two layers of polyhydrated sulfates separated by a

monohydrated layer in Capri Chasma, the rehydration hypothesis seems difficult to apply. We would have to find an explanation for the interlayers that were not modified to polyhydrated sulfates. Dehydration of polyhydrated sulfates into monohydrated sulfates does not seem possible at any time on the surface of Mars [Roach *et al.*, 2009]. The diagenetic dehydration of polyhydrated sulfates into monohydrated ones could be a scenario in case of deep burying. However, the occurrence of polyhydrated sulfates stratigraphically below the monohydrated sulfates rules out this possibility. Another possible explanation is that sulfates would have formed directly as monohydrated or polyhydrated sulfates, depending on the environmental and chemical conditions. The fact that they are associated with very morphologically distinct layers supports this hypothesis. They could have formed under different water releases, or climate conditions, or in a chemically different environment.

5.3. Sulfate Timing

[20] Martian sulfates are mainly localized as counterparts of Valles Marineris ILL that correspond to massive Hesperian deposits [Komatsu *et al.*, 1993; Flahaut *et al.*, 2010]. With the major activity of Tharsis volcanoes in the Hesperian period, very active volcanism could be a good source of sulfur at the surface during that time. Liquid water must have been present when the sulfates formed, implying that the climate of the Hesperian was still wet, and possibly warm, considering that monohydrated sulfates form on Earth at moderate temperatures. Valles Marineris could have

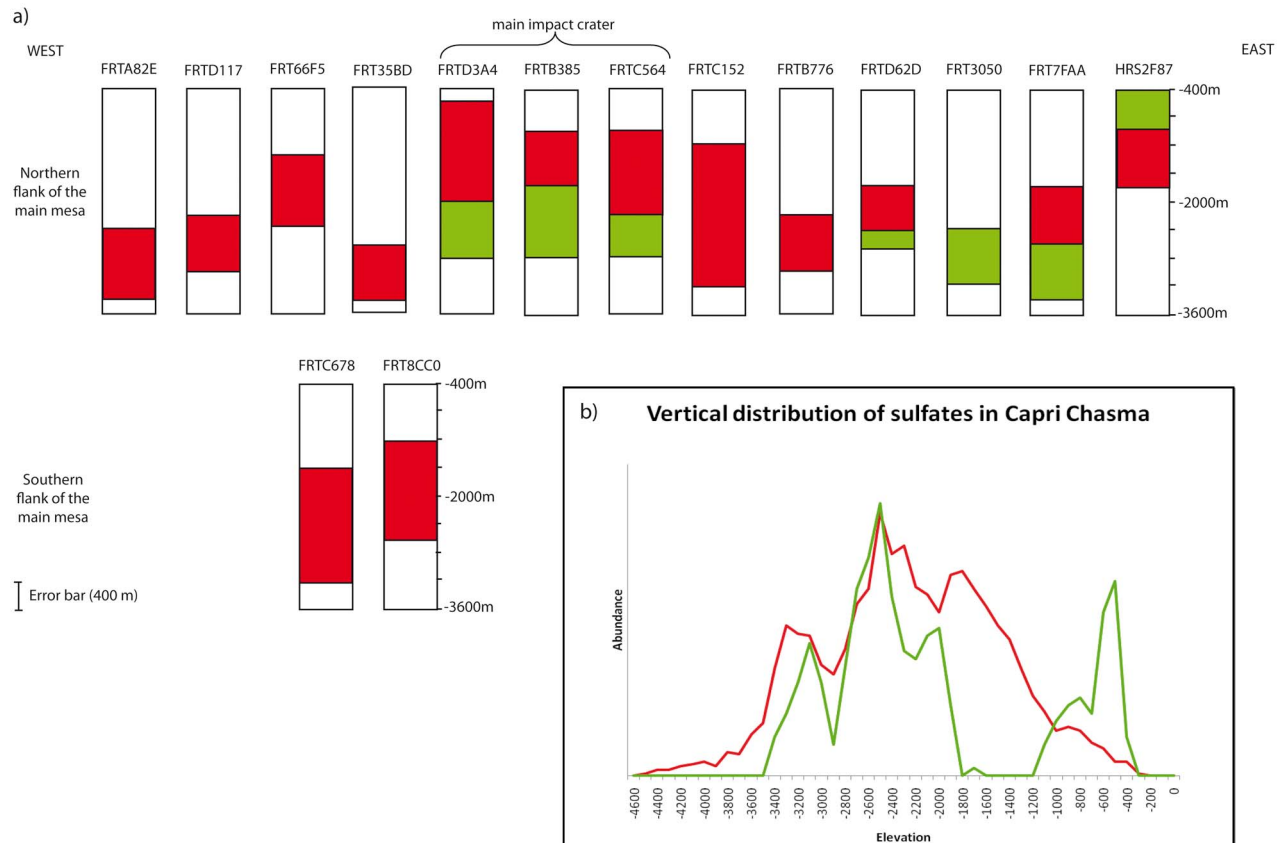


Figure 5. Vertical distribution of CRISM sulfate detections in Capri Chasma. (a) Individual cross-sections of CRISM observations acquired over the main ILD mesa. Red rectangles indicate monohydrated sulfate occurrences; green rectangles indicate polyhydrated sulfate occurrences. Cross-sections are ranked according to their longitude. When the outcrops are too dusty to give any information on the mineralogy, or when the observations are not covering the whole elevation range, the rectangle was left blank. Vertical uncertainty is ~ 400 m, owing to the MOLA data precision. Three observations (FRT0000D3A4, FRT0000B385, FRT0000C564) were taken over the 32 km impact crater of Figure 4 that is affecting the ILD mesa. The impact process may have shifted the elevation of layers from their original level, but the stratigraphic sequence must have been preserved [Flahaut *et al.*, 2010]. (b) Global vertical distribution built on the intersection of the detection maps with the MOLA Digital Topographic Model. Elevation of all the sulfate detection in Capri Chasma are included as an input. Abundances are relative counts of MOLA pixel repeated per elevation interval. Red, monohydrated sulfates; green, polyhydrated sulfates.

been a unique place in space and time to have formed kilometric thick layers enriched in sulfates.

[21] Considering the previous results, with previous morphological observations in Capri Chasma [Flahaut *et al.*, 2010], observations of other ILD in Valles Marineris [Quantin *et al.*, 2005; Fueten *et al.*, 2008; Le Deit *et al.*, 2008; Mangold *et al.*, 2008; Bishop *et al.*, 2009; Murchie *et al.*, 2009a, 2009b], and sulfate contexts on Earth, we can suggest several hypotheses for formation mechanisms of the sulfates in Capri Chasma.

5.4. Sulfate Possible Origins

[22] Sulfates, as is true of other hydrated minerals, require liquid water to form. They are produced in various environments on Earth. Common terrestrial settings include shallow lakes and deep marine basins, periglacial environments,

hydrothermal systems or even acidic rainfalls. Some of these mechanisms can already be ruled out for formation of Martian sulfates according to the surface conditions and morphological observations. In periglacial environments on Earth, the sulfate salts that form a fine, superficial crust are brought by marine and biological aerosols [Bao *et al.*, 2000]. This does not seem possible at any time for Mars. Acidic rainfall is also an unlikely process for Mars as it could not explain the formation of kilometer-thick stacks of sulfate-rich deposits. Hydrothermalism could have occurred on Mars, considering the importance of volcanism there, but the geometry of the deposits does not coincide with this process. On Earth, aside from oceanic ridges, hydrothermal deposits are rather localized and less extensive. Moreover, hydrothermalism would lead to a heterogeneous distribution of the sulfur-rich material, which is not observed in Capri Chasma. On Earth, low-

solubility sulfates, such as gypsum, can also precipitate in deep basins. On Mars, this hypothesis requires warm and wet climatic conditions to allow a large amount of liquid water to fill the canyon during a certain time. This might be difficult to achieve as liquid water was probably limited on the surface of Mars at the beginning of the Hesperian [Bibring *et al.*, 2006; Carr and Head, 2009]. Moreover, if we consider filling the canyon with water in its current topographical setting, the existence of outlets would be a problem, as the canyon is not an isolated basin.

[23] Another idea is that sulfates may have formed secondarily by fluctuation of a groundwater table. This hypothesis has the advantage of not necessarily requiring a wet and warm climate, but it requires groundwater in abundance [Quantin *et al.*, 2005]. The repeated clapping of water tables would have weathered preexisting rocks into sulfates. Alteration of basaltic rocks or ashes that are common on Mars, under acidic conditions, can produce sulfates. Sulfate-free ILD would have been formed first and altered into sulfates later. This hypothesis implies that the primary rocks or the groundwater was sulfur-rich. As the surrounding walls and basalt outcrops in Capri Chasma do not seem weathered, the presence of sulfur-rich water is not likely. Therefore, if sulfates were formed secondarily, they would be the result of the oxidation of a particular sulfur-rich material that formed the preexisting ILD. However, the observed large-scale alternation of polyhydrated and monohydrated sulfates is difficult to explain in this context.

[24] The last possible formation mechanism is the precipitation of evaporites in a shallow body of standing water. This hypothesis does not necessarily require permanent warm and wet conditions. Episodic climate changes could have allowed transient liquid water to be stable on the surface. Recent detailed studies of Valles Marineris's ILD [Okubo, 2010] argue for a sedimentary filling of Valles Marineris during its opening and deepening. Repeated evaporitic sequences precipitated in shallow, standing water progressively during the deepening of the canyon may explain the kilometer-thick sequence of observed sulfates without requiring a large amount of water at the Martian surface. Such a combination of evaporitic deposition and tectonic processes has already been reported on Earth, as in the Danakil kilometer-thick evaporite-rich formation in Ethiopia [Hutchinson and Engels, 1970]. Modification of the environmental and chemical conditions during the process may have formed either monohydrated sulfates or polyhydrated sulfates.

5.5. Origins and Consequences of the Presence of Hydrated Silica

[25] Hydrated silica is found in various environments on Earth. Its main terrestrial formation processes are biological, sedimentary, or volcanic/hydrothermal. As it is associated with sulfates on Mars, the hydrated silica was likely formed in an acidic aqueous environment during the Hesperian or even later [Milliken *et al.*, 2008]. Hydrated silica was observed in situ by the MER rover Spirit in Gusev crater [McLennan, 2003] and from orbit in layered deposits located on the plateaus surrounding Valles Marineris [Milliken *et al.*, 2008; Le Deit *et al.*, 2010]. In Gusev crater, the distribution of hydrated silica is very localized, which is consistent with a very local process of formation such as

hydrothermal activity [McLennan, 2003]. In Capri Chasma, the distribution of hydrated silica is also limited to 2 m scale mounds located on the floor. Hydrated silica in Capri Chasma is detected over the basal polyhydrated-sulfate layer, but at the bottom of the monohydrated sulfate steep cliff. Therefore, if it was once more extended, it would have formed between the deposition of polyhydrated and monohydrated sulfates. As it has not been observed anywhere else in Capri Chasma, and as it is not likely to have such a gap in the formation of sulfates by precipitation, we argue that these hydrated silica-rich mounds could have formed after the setting and the erosion of the sulfate-rich mesa, which is consistent with their current stratigraphic location. Therefore, they could have been formed after 3.5 Gy, which is the age of the opening of Valles Marineris and the beginning of the ILD setting [Flahaut *et al.*, 2010]. If they were once more extended, it must have still been limited to a small area. This argues for a process of formation limited in time and space such as hydrothermalism.

6. Conclusions

[26] We report new detections of sulfates in Capri Chasma and confirm those detected by OMEGA data [Gendrin *et al.*, 2005]. Both types of sulfates, polyhydrated and monohydrated sulfates, are detected. They are associated with alternating layers of distinct albedos and morphological styles. Hydrated silica has also been found locally on the ILD material. The deduced vertical arrangement revealed a large-scale alternation of polyhydrated sulfates/monohydrated sulfates and polyhydrated sulfates. After analyzing and comparing sulfate formation mechanisms on Earth, we show that sulfates in Capri could have been formed by direct precipitation or alteration of preexisting ILDs, either in a shallow open-water basin or by the multiple rises of a groundwater table.

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